

Dark Excitons in Carbon Nanotubes

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We investigate the lowest many-body excited states in carbon nanotubes by means of *ab initio* calculations. On the basis of these calculations and an additional theoretical analysis of the excitons, we demonstrate that the splitting between the dark and bright spin-singlet states is due to the direct Coulomb electron-hole interaction, that the dark exciton always has gerade symmetry, and that it is always lower in energy relative to the bright exciton. Applying these studies to 0.4-0.8-nm-diameter tubes, we find a gerade-ungerade splitting of several tens of an meV, and a singlet-triplet splitting of comparable value. Our symmetry analysis of the origin of the singlet splitting indicates possible strategies to increase the emission efficiency of nanotubes.

In recent years, the luminescence properties of carbon nanotubes have sustained intense theoretical [1, 2, 3] and experimental research [4, 5, 6, 7, 8, 9]. Of particular interest is the study of the emission efficiency and the radiative lifetimes, in view of applications in the field of opto-electronics and photonics [5, 10, 11, 12, 13].

Recent studies on excited-state dynamics [7, 8, 14], combined with the experimentally observed low quantum efficiency, indicate that exciton relaxation is dominated by non-radiative processes, which dramatically quench emission spectra. The presence of optically forbidden states, i.e., *dark* states, below the optical gap, to which the system can decay non-radiatively, is believed to be responsible for the luminescence quenching [1, 13, 15]. Their presence is estimated to increase the effective radiative lifetime of about five times [16]. However, evidence of dark states has been presented only recently in experiments involving large magnetic fields [17], and very little is known about this subject.

Thus far, no theoretical mechanism has been proposed explaining the reason why there are dark states lying below the first bright one nor if this is a general rule for all kinds of tubes.

In this work, we carry out *ab initio* calculations of excitonic states for several tubes of sizes and dimensions of interest in the experimental physics community. On the basis of our calculations, we show that only two pairs of bands are involved in the description of the lowest excitons. This fact, as we shall see later, implies that there is always a dark singlet state below the lowest bright one. Finally, our symmetry analysis allows us to propose alternative ways to increase the quantum efficiency of nanotubes through symmetry-breaking mechanisms.

The excited states are calculated using a many-body theoretical approach which involves both self-energy corrections in the treatment of single-particle energies and effects arising from the electron-hole interaction. The former is treated within the GW approximation [18, 19] while the latter is obtained from the diagonalization of the Bethe-Salpeter Hamiltonian [20, 21, 22, 23].

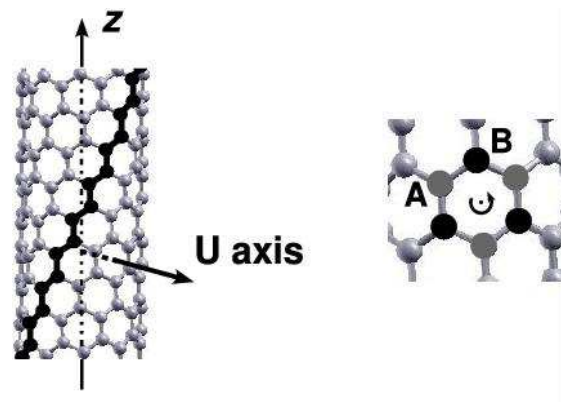


FIG. 1: The two principal symmetries of carbon nanotubes: the roto-translation, RT , with axis z , and the π -rotation about the axis U , R_U . *Left panel:* RT is shown by the dark atoms. The axis U pierces the center of an hexagon and is perpendicular to the screw axis z . *Right panel:* The two inequivalent atoms A and B of each hexagon are shown in greater detail. When R_U is applied to the atomic positions, A goes into B and viceversa.

In our calculations, we take advantage of all the crystal symmetries of the tube (see Fig. 1), which give us a better understanding of the band structure as well as of the excited states [2, 24, 25]. A typical band structure of the tubes, shown in the upper panel of Fig. 2 in the extended zone scheme, has a minimum gap at the points labelled K and K' .

In all the tubes studied, for an energy window from 0 to 5 eV, which is the range of interest for optical absorption experiments, the only transitions that come into play for the lowest singlet states are those between the valence band maximum and the conduction band minimum for k -points near K and K' . In fact, for the singlet states $1u$ and $1g$, where “1” refers to the lowest bound excitonic state and u (g) refers to the parity with respect to π -rotations about the axis U (Fig. 1), most of the weight ($\approx 99\%$) is concentrated near the gap in K and K' . It can be clearly seen in Fig. 2, where the probability

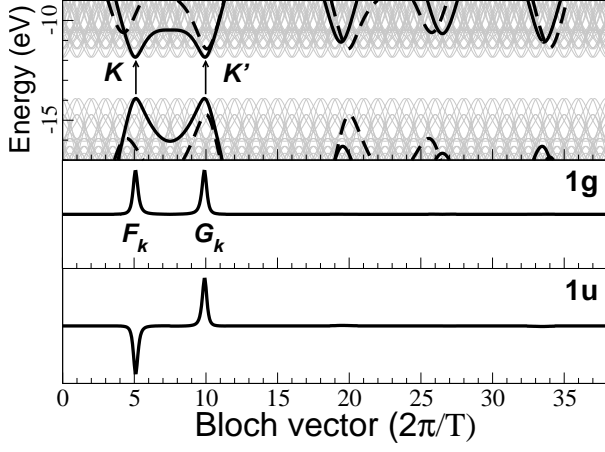


FIG. 2: A typical band structure (upper panel) with the wavefunctions for the two lowest excitons (two lower panels) in the extended zone scheme. Both wavefunctions are localized around K and K' and manifest even and odd parity with respect to the R_U symmetry. The diagrams shown are for the (6,4) tube.

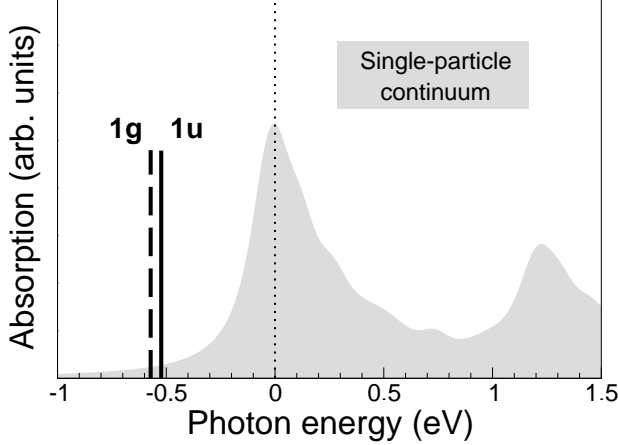


FIG. 3: The lowest singlet states in the absorption spectrum of the (6,4) tube. The shaded line is the single-particle absorption, ignoring excitonic effects. The solid and dotted vertical lines indicate the positions of the two lowest excitons ($1g$ and $1u$), where the lower of the two is dipole forbidden.

amplitude of the transition is plotted as a function of k in the extended zone scheme. In addition, we find that the dark states have the same excitonic composition, as far as the probability amplitude is concerned, since the bright states differ from them only in the phase information (lowest panel in Fig. 2). This behaviour suggests the possibility of describing the lowest excitonic states with a graphite-derived, four-band model.

Let us call the excitonic wavefunction concentrated near K , F_k , and the corresponding wavefunction at K' , G_k . Let the indices i and j denote the space of possible optical transitions $vk \rightarrow ck$ and H_{ij} , the Bethe-Salpeter (BS) Hamiltonian in this space of transitions. F_k and G_k

can be written alternatively in the basis of the transitions as F_i and G_i .

H_{ij} can be decomposed in three parts,

$$H_{ij} = D_{ij} + 2X_{ij} - W_{ij} \equiv D_{ij} + I_{ij}.$$

Here D_{ij} is the diagonal term, X_{ij} is the exchange term, and W_{ij} is the direct Coulomb term. $I_{ij} = 2X_{ij} - W_{ij}$ is the total electron-hole interaction term.

We define the parameters $E = E_{gap} - E_{binding}$ and Δ , as

$$E = \sum_{ij} F_i^* H_{ij} F_j = \sum_{ij} G_i^* H_{ij} G_j \quad (1)$$

and

$$\Delta = \sum_{ij} F_i^* H_{ij} G_j = \sum_{ij} F_i^* I_{ij} G_j. \quad (2)$$

We can obtain excitonic states diagonalizing the matrix

$$M = \begin{pmatrix} E & \Delta \\ \Delta^* & E \end{pmatrix}.$$

It has two eigenvectors, \mathbf{v}_{\pm} , given by

$$\mathbf{v}_{\pm} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \pm \Delta^* / |\Delta| \end{pmatrix}$$

with eigenvalues, $\lambda_{\pm} = E \pm |\Delta|$.

We calculate λ_{\pm} using our *ab initio* BS hamiltonian and model wavefunctions, which take into account only contributions from transitions at k -points very close to K and K' . The splitting $|\Delta|$ is found with an error of no more than 1% with respect to the *ab initio* calculation of the singlet splitting $E_{1u}^S - E_{1g}^S$. We can therefore safely conclude that no bands other than the four graphite-derived ones come into play for the lowest singlet exciton states and the model assumption is correct.

We have yet to demonstrate which of these two states, \mathbf{v}_{\pm} , is bright. In order to simplify the following discussion, note that the direct term W is large compared to the exchange term X , which will therefore be neglected in what follows with an error less than 1 %.

We define the real-space excitonic wavefunction

$$\Psi_K(\mathbf{r}, \mathbf{r}') = \sum_k F_k \phi_{ck}^*(\mathbf{r}) \phi_{vk}(\mathbf{r}'),$$

where $\phi_{ck}^*(\mathbf{r})$ and $\phi_{vk}(\mathbf{r}')$ are the single-particle conduction and valence wavefunctions.

Without loss of generality, we examine only the term with $k = K$, therefore

$$\Psi_K(\mathbf{r}, \mathbf{r}') \approx \phi_{ck}^*(\mathbf{r}) \phi_{vk}(\mathbf{r}').$$

We exclude the modulation factor F_k for simplicity, since the argument below would still be valid. Since the symmetry R_U depicted in Fig. 1 transforms K in K' , and consequently, F_k in G_k , then Eq. 2 can be written as

$$\Delta = \int d^3r \int d^3r' \Psi_K^*(\mathbf{r}, \mathbf{r}') W(\mathbf{r}, \mathbf{r}') \Psi_K(\mathbf{R}_U \mathbf{r}, \mathbf{R}_U \mathbf{r}').$$

If we assume that ϕ_{cK} and ϕ_{vK} are π -like, i.e., are symmetric (π) and antisymmetric (π^*) LCAO combinations of basis functions centered on the two inequivalent atomic sites A and B (which we denote as $\chi_A(\mathbf{r})$ and $\chi_B(\mathbf{r})$), then $\phi_{cK}(\mathbf{r}) = \frac{1}{\sqrt{2}}[\chi_A(\mathbf{r}) - e^{i\delta}\chi_B(\mathbf{r})]$ and $\phi_{vK}(\mathbf{r}) = \frac{1}{\sqrt{2}}[\chi_A(\mathbf{r}) + e^{i\delta}\chi_B(\mathbf{r})]$.

From the relations $\chi_A(\mathbf{R}_{\mathbf{U}}\mathbf{r}) = \chi_B^*(\mathbf{r})$ and $\chi_B(\mathbf{R}_{\mathbf{U}}\mathbf{r}) = \chi_A^*(\mathbf{r})$, we have

$$\Psi_K(\mathbf{R}_{\mathbf{U}}\mathbf{r}, \mathbf{R}_{\mathbf{U}}\mathbf{r}') = -\Psi_K^*(\mathbf{r}, \mathbf{r}').$$

Therefore Δ can be written as

$$\Delta = - \int \int d\mathbf{r} d\mathbf{r}' [\Psi_K(\mathbf{r}, \mathbf{r}')]^2 W(\mathbf{r}, \mathbf{r}').$$

If we define the functions $f(\mathbf{r}) = \frac{1}{2}\{[\chi_A(\mathbf{r})]^2 + e^{2i\delta}[\chi_B(\mathbf{r})]^2\}$ and $g(\mathbf{r}) = e^{i\delta}\chi_A(\mathbf{r})\chi_B(\mathbf{r})$, then Δ can be written as

$$\Delta = \Delta_{AA} + \Delta_{AB},$$

with

$$\begin{aligned} \Delta_{AA} &= - \int d^3r d^3r' [f(\mathbf{r})]^* W(\mathbf{r}, \mathbf{r}') f(\mathbf{r}'), \\ \Delta_{AB} &= - \int d^3r d^3r' [g(\mathbf{r})]^* W(\mathbf{r}, \mathbf{r}') g(\mathbf{r}') \end{aligned}$$

Δ_{AA} is strictly positive and Δ_{AB} is strictly negative. Let the integrated charge of the product of like basis functions be defined as $Q_{AA} = \int d^3r [\chi_A(\mathbf{r})]^2 r$ and for different basis functions $Q_{AB} = \int d^3r \chi_A(\mathbf{r})\chi_B(\mathbf{r})$. Since the product of two gaussians with exponent a centered on two neighboring atoms a distance d apart is a gaussian centered on the midpoint of the two atoms with factor $e^{-ad^2/2}$ and there are three nearest neighbors, then we have, approximately, $Q_{AB} \approx 3e^{-ad^2/2}Q_{AA}$.

Since the dominant exponent for our calculations is 0.2 (a.u.)⁻², the ratio is $3e^{-ad^2/2} = 1.4 > 1.0$. The value of 0.2 (a.u.)⁻² for the exponent a does not depend on the chirality and size of the tube since it is a characteristic only of the local, spatial character of the bonds. Therefore, it should be generally true that the term Δ_{AB} is dominant over Δ_{AA} and, consequently, Δ is negative. We expect the dark state to be generally lower than the bright state for carbon nanotubes, as we see in our *ab initio* calculations for several cases. This is so, because the state \mathbf{v}_+ , which has the higher eigenvalue, E_+ , is an antisymmetric combination of the transitions at K and K' (the relative sign is given by the factor $\Delta^*/|\Delta|$).

For sufficiently long radiative lifetimes, exciton relaxation to triplet states may also become relevant [13]. We therefore briefly discuss the splitting between singlet and dipole-forbidden spin-triplet states.

To calculate such splitting, we perform two BS calculations with two different hamiltonians, one for the singlet state, $H_s = D + 2X - W$, and one for the triplet

(n, m)	d (Å)	$E_{1u}^S - E_{1g}^S$	$E_{1g}^S - E_{1g}^T$	$E_{1u}^S - E_{1u}^T$
(4,2)	4.14	0.090	0.035	0.345
(6,4)	6.83	0.040	0.010	0.130
(8,4)	8.29	0.025	0.005	0.075

TABLE I: Energy splittings in eV. The third, fourth, and fifth columns are the splittings for the $u - g$ singlet states, singlet-triplet for the gerade states and the single-triplet splitting for the ungerade states, respectively.

state, given by $H_t = D - W$. These hamiltonians differ only in the exchange term. Therefore, unlike the dark-bright splitting of the singlet state, which is due to the *direct* Coulomb interaction W , the singlet-triplet splitting is due to the *indirect exchange* Coulomb interaction. Our *ab initio* calculations show that for the triplet states, the even exciton lies above the odd one [i.e., we have $E_{1g}^T > E_{1u}^T$], which is a trend opposite to that found for the singlet states. This behavior has been found also for zig-zag tubes [16]. The above demonstration for singlet states does not apply to the triplet states. This is so because we have found numerically that the simple four-band picture (two pairs of conduction-valence bands) does not hold. In fact, while for the singlet state 99% of the weight is concentrated on the K and K' , for the triplet states at least 6% of the weight is concentrated elsewhere. By evaluating Δ due to these other contributions, we find a positive contribution which is enough to reverse the sign of Δ , forcing the even triplet exciton to lie above the odd one.

The above symmetry analysis of the singlet states suggests new possibilities for increasing the quantum efficiency through symmetry breaking. It can be deduced from the above discussion and perturbation theory that the dark state becomes optically allowed, if the interaction which breaks the symmetry is of the order of magnitude of the splitting $E_u - E_g \approx 0.1$ eV. One way to break the symmetry involves applying external fields. However, their required magnitude may be too large for realistic technological applications, as shown in Ref. [17], where magnetic fields are used. An alternative strategy could involve the use of interacting semiconductor nanotubes. This is suggested by recent theoretical work on excitons in polymeric crystals, where interactions between different polymeric chains were shown to control the splitting between dark and bright excitons [26, 27]. We have therefore reason to believe that bundles or arrays of *semi-conducting* nanotubes could be examples of systems with increased quantum efficiency and possible candidates of interest for practical devices.

In conclusion, we have provided theoretical and numerical proof, using an *ab initio*, many-body approach, and separately, a four-band model, that dark excitonic states in semiconducting single-walled nanotubes exist,

that they have even \mathbf{R}_U symmetry, and that they are always below the corresponding bright state. Furthermore, the dark-bright energy for tubes in the diameter range of 0.4 - 0.8 nm is some tens of meV with decreasing value as the tube radius increases. We show that these results come from a four-band picture and that the splitting is due to the direct Coulomb interaction between the electron-hole and the matrix element of the inter-valley interaction. We also calculate the singlet-triplet splitting. Here we find results of the same order of magnitude and the same decreasing trend with increasing radius as in the case of the dark-bright splitting. Finally, we have proposed, on the basis of the symmetry characteristics of the dark state, coupled semiconductor nanotubes as systems where the symmetry breaking induced by the intertube interaction leads to increased quantum efficiency.

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